0.50, CH_2Cl_2); TLC R_f 0.48 (solvent B); IR (CCl_4) ν 2780, 2675, 1715, 1700, 1530, 1350 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.62 (s, 1 H, CHO), 6.23 (m, 2 H, H-2,3), 4.74 (dd, 1 H, $J_{4,5endo} \sim 0$ Hz, $J_{5endo,6exo} = 3.4$ Hz, $J_{5endo,7syn} = 1.1$ Hz, H-5endo), 3.74 (t, 1 H, $J_{1,6exo} = 3.5$ Hz, H-6exo), 3.56 (m, 1 H, H-4), 3.47 (m, 1 H, H-1), 1.95 (br d, 1 H, $J_{7syn,7anti} = 9.4$ Hz, H-7anti), and 1.79 (dd, 1 H, H-7syn); ^{13}C NMR (50.31 MHz, $CDCl_3$) δ 197.8 (CHO), 137.8 (C-2), 134.8 (C-3), 84.7 (C-5), 58.6 (C-6), 49.9 (C-4), 47.2 (C-7), and 43.4 (C-1).

(5*S*,6*S*)-1-*C*-(5-*exo*-Nitrobicyclo[2.2.1]hept-2-en-6-*endo*-yl)carboxaldehyde (3). Compound **3** (enantiomer of **2**) was prepared from **3e** or **3f** by the procedure above mentioned: $[\alpha]_D$ +86° (*c* 1.60, CH_2Cl_2).

(5*R*,6*R*)-1-*C*-(5-*endo*-Nitrobicyclo[2.2.1]hept-2-en-6-*exo*-yl)carboxaldehyde (4). Compound **4** was prepared from **4d**: $[\alpha]_D$ -88° (*c* 2.80, CH_2Cl_2); TLC R_f 0.58 (solvent B); IR (CCl_4) ν 2820, 2680, 1715, 1700, 1530, 1355 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.84 (s, 1 H, CHO), 6.53 (br dd, 1 H, $J_{1,2} = 3.1$ Hz, $J_{2,3} = 5.4$ Hz, H-2), 6.17 (br dd, 1 H, $J_{3,4} = 2.7$ Hz, H-3), 5.48 (t, 1 H, $J_{4,5exo} = J_{5exo,6endo} = 3.6$ Hz, H-5exo), 3.64 (m, 1 H, H-4), 3.33 (m, 1 H, H-1), 3.22 (dd, 1 H, $J_{6endo,7syn} = 2.1$ Hz, $J_{1,6endo} \sim 0$ Hz, H-6endo), 1.64 (br dd, 1 H, $J_{7syn,7anti} = 9.5$ Hz, H-7anti), and 1.42 (br dd, 1 H, H-7syn); ^{13}C NMR (50.31 MHz, $CDCl_3$) δ 197.8 (CHO), 138.7 (C-2), 134.4 (C-3), 84.2 (C-5), 57.0 (C-6), 47.0 (C-4), 45.5 (C-7), and 44.3 (C-1).

(5*S*,6*S*)-1-*C*-(5-*endo*-Nitrobicyclo[2.2.1]hept-2-en-6-*exo*-yl)carboxaldehyde (5). Compound **5** (enantiomer of **4**) was obtained from **5d**, **5e**, or **5f**: $[\alpha]_D$ +90° (*c* 2.50, CH_2Cl_2).

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Registry No. **2**, 123003-29-2; **2a**, 119448-02-1; **2b**, 119479-77-5; **2c**, 119479-80-0; **2d**, 123050-38-4; **3**, 123050-43-1; **3a**, 119479-74-2; **3b**, 119479-78-6; **3c**, 119479-81-1; **3e**, 123050-39-5; **3f**, 123050-42-0; **4**, 123050-44-2; **4a**, 119479-75-3; **4b**, 119479-79-7; **4c**, 119479-82-2; **4d**, 123003-28-1; **5**, 123050-45-3; **5a**, 119479-76-4; **5b**, 119565-81-0; **5c**, 119479-83-3; **5d**, 123050-37-3; **5e**, 123050-40-8; **5f**, 123050-41-9.

Coupling Reactions of *O*-(Trimethylsilyl) Glycosides and 6-*O*-(*tert*-Butyldiphenylsilyl)-Protected Galactosides in the Presence of Trimethylsilyl Triflate. A New Method of Forming β-(1→6)-Oligosaccharidic Linkages†

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Introduction

Our studies with monoclonal IgA's, having specificity for β-(1→6)-D-galactopyranans,[1] prompted a synthesis of β-(1→6)-linked oligosaccharides. Recently we reported[2] a method for the synthesis of (1→6)-β-D-galactopyranooligosaccharides. The method involves the selective protection of the 6-hydroxyl group of β-D-galactopyranosides with the *tert*-butyldiphenylsilyl group, followed by acylation of the remaining hydroxyls, selective de-*O*-silylation, and coupling of the resulting nucleophile with a suitable α-D-galactosyl halide. However, de-*O*-silylation with a solution of 3% hydrogen chloride proved[2] to be troublesome when acetyl groups or other, acid-sensitive functions were present.

Herein, a method for a stereospecific coupling of 6-*O*-*tert*-butyldiphenylsilyl-protected galactopyranosides with *O*-(trimethylsilyl) glycosides in the presence of trimethylsilyl trifluoromethanesulfonate[3] (abbreviated trimethylsilyl triflate, TMS triflate, TMSOTf) is presented. In this case, the silyl moiety allows the direct coupling, without a prior deprotection step.

Results and Discussion

Trimethylsilyl triflate, apart from being a powerful silylating agent, also catalyzes a wide variety of reactions. It has been used as a catalyst in reactions of acetals with trialkylallylsilanes to form new carbon–carbon bonds,[4] in reactions of acetals with trimethylsilyl glucosides to yield glucosides with 1,1′-diacetal structure[5] and has also been used in coupling reactions leading to the synthesis of nucleosides[6] as well as oligosaccharides.[7] In addition, TMSOTf has been used by Murata and Noyori[8] for the transetherification of silylated ethers and by Tietze et al.[9] for the synthesis of aryl glucosides from trimethylsilyl glucoside and silylated aromatic ethers. All this prompted us to examine the possibility of employing TMS triflate for oligosaccharide synthesis using two sugar units selectively protected at C-1 and C-6 with silyl groups.

Trimethylsilyl β-D-glycosides **1** (see Table I) reacted smoothly with 6-*O*-(*tert*-butyldiphenylsilyl)-protected mono- and trigalactopyranosides **2** in the presence of trimethylsilyl triflate to give β-linked di- and tetraoligosaccharides in good yields (entries a, b, c, e). The anomeric trimethylsilyl α-D-galactoside (entry c-α) and methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside[2] also gave the β-linked disaccharide **3c** under the same conditions, but the yield was substantially lower.

To obtain the disaccharide ligand **3d** for photoaffinity labeling studies, the 6-*O*-(*tert*-butyldiphenylsilyl) derivative (**2d**) of 3-azi-1-methoxybutyl β-D-galactopyranoside[10] was prepared[2] and coupled with peracetylated trimethylsilyl β-D-galactopyranoside[10] in the presence of TMSOTf (entry d). In spite of some decomposition of the starting azimethoxybutyl galactoside, desired disaccharide **3d** was isolated in 54% yield.

The described coupling reactions occur under relatively mild conditions, in aprotic solvents, at -30 to -70 °C, and this allows the use of synthetic intermediates that are protected with acetyl, benzoyl, or *p*-phenylbenzoyl groups. The latter can be easily removed as we showed in the case of **3e**, yielding the unprotected tetrasaccharide **4e**.

In conclusion: the coupling of two silyl-protected saccharide units **1** and **2** in the presence of trimethylsilyl

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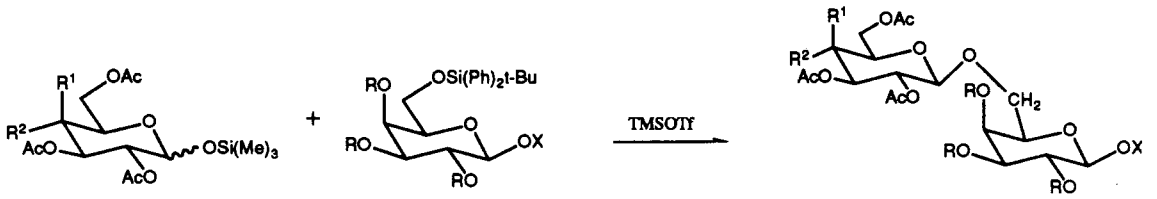
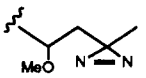
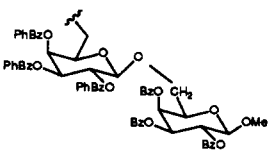
Table I



	1			2						mole ratio to 2	
entry	R^1	R^2	α,β	R	X	solvt	time, days	temp, °C	yield, %	1	TMSOTf
a	H	OAc	β	Ac	Me	CH_2Cl_2	3	−70 to −30	70	1.3	0.7
b	H	OAc	β	Bz	Me	CH_2Cl_2	2	−70 to −30	74	1.3	0.6
c	OAc	H	β	Bz	Me	$C_2H_4Cl_2$	2	−50 to −30	76	1.1	0.5
c-α	OAc	H	α	Bz	Me	$C_2H_4Cl_2$	2	−50 to −30	47	1.3	0.5
d	OAc	H	β	Bz		CH_2Cl_2	8	−78	54	1.4	0.75
e	H	OAc	β	Bz		CH_2Cl_2	8	−78	72	1.6	1.5

triflate constitutes a new method of forming (1→6)-β-D-intersaccharide linkages, which bypasses the usual deprotection step. Both substrates, 6-*O*-*tert*-butyldiphenylsilylated methyl β-D-galactosides[2,11] (or -glucosides[12]) and trimethylsilyl glycosides[13] are easily accessible, which in combination with relatively mild reaction conditions makes the procedure attractive. The method is particularly advantageous when acetyls are the protecting group of choice and is compatible with the presence of sensitive functionalities such as diazirino and acetal moieties.

Experimental Section

Melting points are uncorrected. NMR spectra (^1H and ^{13}C) were recorded in $CDCl_3$ solution with a Varian XL-300 spectrometer, using Me_4Si as the internal standard. Proton spectra of all new compounds were interpreted by first-order analysis or, when necessary, by homonuclear selective decoupling. Carbon signals were assigned by comparison with data of similar compounds[2,10] or by two-dimensional ^1H–^{13}C shift-correlation spectra. Optical rotations were measured with a Perkin-Elmer 241 MC automatic polarimeter. Mass spectra were recorded with a ^{252}Cf plasma desorption mass spectrometer. TLC was carried out on silica gel GHLF (Analtech), and flash chromatography was performed with columns of silica gel 60 (Merck, 230–400 or >400 mesh) with the following eluting solvents: A, toluene/acetone; B, carbon tetrachloride/acetone; C, *n*-hexane/ethyl acetate; D, toluene/ethyl acetate.

All reactions were carried out under argon in dry solvents. Nonaqueous solutions obtained during workup procedures were dried over magnesium sulfate and concentrated under reduced pressure at <40 °C.

3-Azi-1-methoxybutyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside (2d). 3-Azi-1-methoxybutyl β-D-galactopyranoside[10] (0.14 g, 0.48 mmol) was dissolved in tetrahydrofuran (1 mL) containing pyridine[14] (0.15 mL, 1.92 mmol), and *tert*-butyldiphenylsilyl chloride (0.25 mL, 0.96 mmol) was added at room temperature. The mixture was stirred (~3 h) until all substrate was converted to one less polar product [TLC, solvent C (1:2)]. Pyridine (0.35 mL, 4.32 mmol), benzoyl chloride[15] (0.5 mL, 4 mmol), and a catalytic amount of 4-(dimethylamino)pyridine were added, and the mixture was stirred at room temperature until the benzoylation was complete [TLC, solvent C (1:1)]. The reaction was quenched by addition of ice water, and the organic layer was diluted with dichloromethane, washed successively with water, aqueous sodium bicarbonate, and water again, dried, and concentrated. Column chromatography [solvent C (2:1)] gave **2d**: 0.36 g (89%); $[\alpha]_D$ +55.6° (*c* 0.8, $CHCl_3$); ^1H NMR δ 6.01–6.04 (m, 1 H, H-4 of two isomers), 5.60–5.86 (m, 2 H, H-2,3 of two isomers), 4.87–5.33 (m, 2 H, H-1, H-α of two isomers), 3.76–4.12 (m, 3 H, H-5,6,6a of two isomers), 3.14–3.15 (2 s, 3 H, OCH_3 of two isomers), 1.49–1.74 (m, 1 H, H-β of two isomers), 0.99–1.07 (m, 12 H, C γ-CH_3, $SiC(CH_3)_3$ of two isomers); ^{13}C NMR δ 101.8, 98.9 (C-α of two isomers), 97.5, 97.3 (C-1 of two isomers), 74.0–74.6 (C-5 of two isomers), 72.1 (C-3), 69.7, 69.9 (C-2 of two isomers), 67.9, 68.0 (C-4 of two isomers), 61.4, 63.4 (C-6 of two isomers), 52.4 (OCH_3), 39.0, 39.1 (C-β of two isomers), 26.7, 26.8 [$SiC(CH_3)_3$ of two isomers], 23.0, 23.1 (C-γ of two isomers), 20.1 (CH_3), 19.0, 19.2 [$SiC(CH_3)_3$ of two isomers]. Anal. Calcd for $C_{48}H_{50}O_{10}N_2Si$: C, 68.39; H, 5.98; N, 3.32. Found: C, 68.34; H, 5.82; N, 3.27.

Trimethylsilyl 2,3,4,6-Tetra-*O*-acetyl-α- and -β-D-galactopyranoside (1c-α and 1c). 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranose[10] (7 g, 20 mmol) was suspended in ethyl ether (100 mL), and hexamethylsilazane (4.2 mL, 20 mmol), chlorotrimethylsilane (3 mL, 24 mmol), and pyridine (1.6 mL, 20 mmol) were added successively, with stirring. After 1 h at room temperature reaction was completed [TLC, solvent D (7:3)], and the white precipitate was removed by filtration. Concentration of the filtrate, followed by column chromatography [solvent C (4:1)] gave **1c-α**: 0.34 g (4%); mp 116–117 °C; $[\alpha]_D$ +124.7° (*c* 0.5, $CHCl_3$); ^1H NMR δ 5.41–5.43 (m, 2 H, H-1,4), 5.34 (dd, 1 H, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 10.7 Hz, H-3), 5.04 (dd, 1 H, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 10.7 Hz, H-2), 4.34 (m, 1 H, H-5), 4.06 (m, 2 H, H-6,6a), 1.98–2.12 (4 $COCH_3$), 0.15 (s, 9 H, $Si(CH_3)_3$). Anal. Calcd for $C_{17}H_{28}O_{10}Si$: C, 48.56; H, 6.71. Found: C, 48.72; H, 6.75.

Eluted next was **1c**: 7.3 g (87%), colorless syrup; physicochemical data in agreement with ref 10.

General Procedure for Coupling Reactions. After cooling to the desired temperature, the first portion (10% of the total

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(14) *N,N*-Dimethylformamide and silver nitrate can be used instead of tetrahydrofuran and pyridine.
(15) Acetic anhydride (0.41 mL, 4.32 mmol) can be added instead of benzoyl chloride, and after coevaporation three times with toluene to dryness 3-azi-1-methoxybutyl 2,3,4-tri-*O*-acetyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside can be obtained (91% yield).

amount used) of TMSOTf was added to a solution of 6-*O*-(*tert*-butyldiphenylsilyl) derivative **2**, and the first portion (one-third of the total amount used) of trimethylsilyl glycoside **1** dissolved in the appropriate solvent (see Table I for details). The reaction was followed by TLC, and subsequent portions of glycoside **1** and TMS triflate were added periodically. When the reaction was complete, the reaction mixture was neutralized with triethylamine, diluted with dichloromethane, washed with water, aqueous sodium bicarbonate, and water again, and dried. Concentration, followed by column chromatography yielded products **3a–e** listed below.

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-acetyl-β-D-galactopyranoside (3a): prepared from methyl 2,3,4-tri-*O*-acetyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside[2] (**2a**; 0.056 g, 0.1 mmol) and trimethylsilyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside[10] (**1a**; 0.055 g, 0.13 mmol); TLC, solvent A (7:2). Column chromatography [solvent B (4:1)] gave **3a**: 0.046 g (70%); mp 121–122 °C (lit.[16] mp 122 °C); ^{1}H NMR δ 5.37 (br d, 1 H, $J_{3,4}$ = 3.2 Hz, H-4), 4.94–5.21 (m, 5 H, H-2,2′,3,3′,4′), 4.58 (d, 1 H, $J_{1',2'}$ = 8.1 Hz, H-1′), 4.38 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1), 4.13–4.31 (m, 2 H, H-6,6a′), 3.65–3.97 (m, 4 H, H-5,5′,6,6a), 3.53 (s, 3 H, OCH_3).

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (3b): obtained from methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside[2] (**2b**; 0.37 g, 0.5 mmol) and **1a** (0.27 g, 0.65 mmol); TLC, solvent A (7:1). Column chromatography [solvent A (10:1)] gave **3b**: 0.31 g (74%); $[\alpha]_D$ + 92.3° (*c* 0.8, $CHCl_3$); ^{1}H NMR δ 5.69 (br d, 1 H, $J_{3,4}$ = 3.4 Hz, H-4), 5.58 (dd, 1 H, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 10.4 Hz, H-2), 5.38 (dd, 1 H, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 10.4 Hz, H-3), 4.81–5.04 (m, 3 H, H-2′,3′,4′), 4.52 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1′), 3.48–4.04 (m, 6 H, H-5,6,6a,5′,6′,6a′), 3.43 (s, 3 H, OCH_3); ^{13}C NMR δ 102.4 (C-1), 100.7 (C-1′), 73.2, 73.8 (C-5,3′), 71.9, 71.8, 71.2 (C-3,2′,5′), 69.7 (C-2), 68.6, 68.3, 68.1 (C-4,6,4′), 61.8 (C-6′), 57.2 (OCH_3). Anal. Calcd for $C_{42}H_{44}O_{18}$: C, 60.28; H, 5.3. Found: C, 59.99; H, 5.27.

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (3c): (a) prepared from **2b** (0.3 g, 0.4 mmol) and trimethylsilyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside[10] (**1c**, 0.18 g, 0.43 mmol); TLC, solvent A (7:1). Column chromatography [solvent A (10:1)] gave **3c**: 0.26 g (76%); mp 214–215 °C (lit.[17] mp 215–216 °C); ^{1}H NMR and ^{13}C NMR spectral data are in agreement with the literature,[17] except for the joint assignment of carbon signals at 70.8 and 70.9 to C-3′,5′, which were misprinted as assigned to C-5,3′. (b) Obtained from **2b** (0.224 g, 0.3 mmol) and trimethylsilyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside (**1c-α**, 0.16 g, 0.38 mmol); TLC, solvent A (7:1). Column chromatography [solvent A (10:1)] gave **3c**: 0.12 g (47%).

3-Azi-1-methoxybutyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (3d): obtained from 3-azi-1-methoxybutyl 2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside (**2d**, 0.067 g, 0.08 mmol) and **1c** (0.047 g, 0.11 mmol); TLC, solvent C (3:1) gave **3d**: 0.04 g (54%); mp 123–125 °C; $[\alpha]_D$ +122.6° (*c* 0.8, $CHCl_3$); ^{1}H NMR δ 5.93–6.03 (m, 2 H, H-2,4 of two isomers), 5.63–5.73 (m, 2 H, H-1,3 of two isomers), 5.37 (br d, 1 H, $J_{3',4'}$ ~ 3.3 Hz, H-4′), 5.19 (dd, 1 H, $J_{1',2'}$ = 7.9 Hz, $J_{2',3'}$ = 10.3 Hz, H-2′), 5.02 (dd, 1 H, $J_{2',3'}$ = 10.3 Hz, $J_{3',4'}$ = 3.3 Hz, H-3′), 4.90–4.94 and 4.54–4.58 (2 m, 1 H, H_α of two isomers), 4.66–4.74 (m, 1 H, H-5 of two isomers), 4.52 (d, 1 H, $J_{1',2'}$ = 7.9 Hz, H-1′), 3.74–4.15 (m, 5 H, H-6,6a,5′,6′,6a′), 3.14 and 3.37 (2 s, 3 H, OCH_3 of two isomers), 1.98, 2.01, 2.09 and 2.16 (4 OAc), 1.57–1.83 (m, 1 H, H_β of two isomers), 1.02 and 1.18 (2 s, 3 H, CH_3 of two isomers); ^{13}C NMR δ 98.1 and 102.3 (C_α of two isomers), 101.1 and 101.3 (C-1′ of two isomers), 92.9 and 93.1 (C-1 of two isomers), 70.8, 70.9, 71.0 (C-3′,5′ of two isomers), 68.2, 68.3, 68.4, 68.6, 68.8, 69.0, 69.4, 69.5 (C-2,3,4,5,6,2′ of two isomers), 67.0 (C-4′), 61.2 (C-6′), 52.1, 55.9 (OCH_3 of two isomers), 38.8, 38.9 (C_β of two isomers), 23.2 (C_γ of two isomers), 20.7 ($COCH_3$), 20.3 (C_γ-CH_3). Anal. Calcd for $C_{46}H_{50}N_2O_{19}$: C, 59.10; H, 5.39; N, 3.00. Found: C, 59.02; H, 5.45; N, 3.21.

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Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-*O*-[2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-β-D-galactopyranoside (3e): prepared from methyl *O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranosyl]-(1→6)-*O*-[2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside[2] (**2e**; 0.192 g, 0.1 mmol) and **1a** (0.067 g, 0.16 mmol); TLC, solvent A (10:1) or B (9:2). Column chromatography [solvent A (15:1)] gave **3e**: 0.146 g (72%); mp 163–165 °C; $[\alpha]_D$ +200.0° (*c* 0.6, $CHCl_3$); ^{1}H NMR δ 5.79, 5.87, 5.99 (3 br d, 3 H, $J_{3,4}$ = $J_{3',4'}$ = $J_{3'',4''}$ ~ 3.4 Hz, H-4,4′,4″), 5.43–5.76 (m, 6 H, H-2,3,2′,3′,2″,3″), 4.81–5.14 (m, 3 H, H-2‴,3‴,4‴), 4.83 (d, 1 H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.59, 4.62 (2 d, 2 H, $J_{1,2}$ = $J_{1'',2''}$ = 7.9 Hz, H-1,1″), 4.08 (d, 1 H, $J_{1''',2'''}$ = 7.8 Hz, H-1‴), 3.63–4.20 (m, 12 H, H-5,6,6a,5′,6′,6a′,5″,6″,6a″,5‴,6‴,6a‴), 3.30 (s, 3 H, OCH_3), 1.92–2.04 (4 s, 12 H, 4 OAc); ^{13}C NMR δ 102.2 (C-1), 100.4, 100.7, 101.2 C-1′,1″,1‴), 72.3, 72.7, 72.9 (C-5,5′,5″), 71.1, 71.7 (2 C), 71.8 (2 C), (C-3,3′,3″,3‴,5‴), 69.8 (2 C), 70.0 (C-2,2′,2″), 66.2, 67.2, 67.7, 68.0 (2 C), 68.1, 68.6 (C-4,6,4′,6′,4″,6″,2‴,4‴), 61.7 (C-6‴), 56.8 (OCH_3), 20.5, 20.6 ($COCH_3$). Anal. Calcd for $C_{114}H_{100}O_{34}$: C, 67,99; H, 5.00. Found: C, 67.66; H, 5.14.

De-O-acylation of tetrasaccharide **3e** [0.05 g, 0.025 mmol; $NaOCH_3$, methanol–toluene (5:1), pH ~ 9, 60 °C, 24 h] gave, after purification (HPLC: Zorbax-NH_2, 5% CH_3CN/H_2O), methyl *O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-galactopyranosyl-(1→6)-*O*-β-D-galactopyranosyl-(1→6)-β-D-galactopyranoside (**4e**): 0.017 g (82%); MS (Cf) $[M + Na]^+$ 703.2 (calcd for $C_{25}H_{44}O_{21}$: MS 680.237).

Registry No. **1a**, 19126-95-5; **1c**, 117405-70-6; **1c-α**, 123163-89-3; **2a**, 110319-38-5; **2b**, 110319-39-6; **2d** isomer 1, 123076-15-3; **2d** isomer 2, 123076-20-0; **2d** deprotected deriv isomer 1, 117405-74-0; **2d** deprotected deriv isomer 2, 117405-77-3; **2e**, 110319-60-3; **3a**, 97058-67-8; **3b**, 123076-16-4; **3c**, 108999-02-6; **3d** isomer 1, 123076-17-5; **3d** isomer 2, 123163-90-6; **3e**, 123076-18-6; **4e**, 123076-19-7; 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranose, 70191-05-8.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) Oxidation of Silyl Enol Ethers to Enones via DDQ–Substrate Adducts

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Recently we reported[1] that the reaction of silyl imidates of the 4-aza-3-keto steroids with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) affords Δ^1-lactams via unprecedented adduct formation between the substrate and quinone followed by an electrocyclic reaction to establish the unsaturation. Oxidation of ketones to enones via reaction of their silyl enol ethers with DDQ was believed to involve allylic hydride abstraction to afford an oxygenated allylic cation which furnishes enone on workup.[2] Reinvestigation of this reaction has now established the intermediacy of substrate–quinone adducts.

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